SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

PROTOCOL FOR THE PERIODIC MONITORING OF NITROGEN OXIDES, CARBON MONOXIDE, AND OXYGEN FROM STATIONARY ENGINES SOURCES SUBJECT TO SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT RULE 1110.2

July 24, 2007 APRIL 13, 2005

ENGINEERING AND COMPLIANCE DIVISION INDUSTRIAL BRANCH

SOURCE TEST ENGINEERING BRANCH MONITORING & ANALYSIS

PROTOCOL FOR THE PERIODIC MONITORING OF NITROGEN OXIDES, CARBON MONOXIDE, AND OXYGEN FROM SOURCES SUBJECT TO SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT RULE 1110.2

1.0 OVERVIEW AND APPLICABILITY

This protocol is applicable to the determination of nitrogen oxides (NO and NO₂), carbon monoxide (CO), and oxygen (O₂) concentrations in emissions from engines subject to South Coast Air Quality Management District (AQMD) Rule 1110.2 using portable electrochemical (EC) analyzers. This protocol is limited to engines that use fuels such as natural gas, propane, butane, gasoline, landfill gas, digestor gas, refinery gas and fuel oils and relies upon EPA Conditional Test Method CTM-030 (see Attachment I). Deviations from CTM-030 have been adopted in order to simplify the procedure, while still providing a reasonable assurance of compliance. When CTM-030 and this protocol are in disagreement, this protocol shall supercede. This protocol is not intended to replace the EPA reference methods of 40 CFR Part 60, Appendix A, or AQMD source test methods, but rather to facilitate the measurement of emissions on a periodic monitoring schedule. These test results, along with other pertinent information, may be considered by AQMD as credible evidence of compliance or non-compliance with Rule 1110.2. AQMD reserves the right to modify this protocol without advance notice.

When engines subject to Rule 1110.2 cannot be tested using this protocol, the protocol may be modified following written approval of the Executive Officer. The latest version of the protocol can be found on the AQMD web site.

2.0 MEASUREMENT SYSTEM PEFORMANCE SPECIFICATIONS AND APPARATUS

Use any measurement system that meets the performance and design specifications in Sections 4 and 5 of CTM-030 and the requirements of this protocol. The measurement system shall maintain the gas sample at conditions that will prevent condensation in the lines or when it contacts the <u>electrochemicalEC</u> cells. Additions to, or modifications of, vendor supplied electrochemical analyzers (e.g. heated sample lines, thermocouples, flow meters, etc.) may be required to meet the specifications indicated in this protocol.

2.1 SENSITIVITY

The minimum detectable limit depends on the nominal range and resolution of the electrochemical cell and signal to noise ratio of the measurement system. For the CO, NO, and NO₂ electrochemical cells, the minimum detectable limit shall be less than or equal to 3 percent of the selected range (see Section 3.1) or 1 ppm, whichever is less restrictive. For the O₂ electrochemical cell, the minimum detectable limit shall be less than or equal to 0.3 percent O₂.

2.2 INTERFERENCE RESPONSE

The CO, NO, and NO₂ interference response must be less than or equal to \pm 5 percent of the span gas concentration. Refer to Section 7.7 of CTM-030 for the calculation method. Analyzers that have been verified for interference response by a recognized agency (e.g. ETV or TUV), or as approved by EPA Method 301 verification, shall be considered in compliance with this interference check specification.

An NO and NO₂ interference response of the CO electrochemical cell shall be performed during each calibration check by using the CO interference response procedure listed in CTM-030 6.3.1. The interference response check shall be performed by injecting a NO span gas, balance nitrogen, to determine the positive response by the CO electrochemical cell. Then a NO₂ span gas in either balance nitrogen or air is inserted into the CO electrochemical cell to determine the positive interference response by the CO cell.

Notwithstanding the interference checks required by CTM-030, an annual interference check of the NO and NO_2 electrochemical cells shall be performed for combustion devices which have a potential to emit SO_2 concentrations greater than 10 ppm. The interference check procedure shall consider both positive and negative biases in the data, and shall demonstrate (using an equation similar to that in Section 6.3.1 of CTM-030) that the combined NO and NO_2 interference responses due to SO_2 contribute less than 5 percent of the NO_x concentration in the emissions. The facility shall justify the SO_2 concentration selected for interference verification using historical data or mass balance calculations.

The potential for interference from other flue gas constituents should be reviewed with the electrochemical analyzer manufacturer based on site-specific data.

2.3 MOISTURE REMOVAL SYSTEM

A chilled condenser or similar device to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas shall be required if the NO_2 portion of NO_x (based on average test data collected according to an approved source test or this protocol) is greater than 10 percent. Alternatively, for gas streams with less than 10 percent NO_2 a device that uses ambient means to condense moisture from the gas stream before the electrochemical cells is acceptable for this protocol. All sampling system components shall be non-reactive with nitrogen dioxide,

2.4 ELECTROCHEMICAL CELL TEMPERATURE INDICATOR

The analyzer shall be equipped with a temperature measurement device to monitor the electrochemical cell temperature. The temperature may be monitored at the surface, within the cell, or in close proximity to the cells such that it indicates the operating temperature of the cells. At no time shall the analyzer be used outside the manufacturer's recommended operating range.

2.5 DATA RECORDER

The data shall be recorded using procedures in Section 5.1.10 of CTM-030. The data recorder must allow each data point to be read at least once every 15 seconds.

2.6 CALIBRATION ASSEMBLY

A three-way valve assembly, tee, or equivalent for introducing calibration gases at ambient pressure to the sample probe during calibration checks. The assembly shall be designed such that only calibration gas is processed and that calibration gases flow through all gas path filters. Figure 1 is a diagram of the calibration assembly.

3.0 MEASUREMENT SYSTEM PERFORMANCE CHECK PROCEDURES

The following procedures define the steps to follow in order to verify measurement system performance and accuracy. For each set of field emissions tests, perform a successful <u>interference test (Section 2.2)</u>, pre-test (Section 3.<u>3</u>2) and post-test calibration check (Section 3.<u>4</u>3) within ten calendars days. Conduct a linearity check (Section 3.<u>5</u>4) and stability check (Section 3.<u>6</u>5) every 12 months, or more often, as necessary, to ensure proper operation of the electrochemical cells.

For gas streams where the NO_2 portion of <u>total</u> NO_x is less than or equal to 10 percent (based on average test data collected according to an approved source test or this protocol), use of the NO_2 electrochemical cell is voluntary.

3.2 CALIBRATION GAS

Use EPA Protocol $\underline{2}1$ gases or NIST traceable calibration gases, which are certified to a minimum accuracy of \pm 2 percent, or NIST traceable calibration gases. Fresh air, which is defined as air free from ambient CO, NO_x, and other pollutants, is permitted for O₂ calibration, at $-(20.9\% O_2)$, and as a zero gas for CO and NO_x. The instrument and the electrochemical cell design will determine the analytical range for each gas component.

Select a span calibration gas concentration, (span gas₂) that is within the analytical range for each of the CO, NO, and NO₂ electrochemical cells, such that the expected average stack gas readings for each test are between 25 and 150 percent of the span gas selected. The nominal range is defined as zero to the span gas selected. Fresh air, (20.9 percent O_2) may be used for the O_2 span gas.

3.3 PRE-TEST CALIBRATION CHECK

Assemble the measurement system by following the manufacturer's recommended procedures for preparing and preconditioning the gas analyzer. Assure the system has no leaks by plugging the probe tip and observing that the sample flow rate goes to zero, and verify the gas scrubbing agent is not depleted. Energize sample pump and allow portable electrochemical analyzer to warm up to ambient temperature. Conduct the following procedures for each electrochemical cell within 10 calendar days of each set of the field emissions tests and the post-test calibration check.

3.3.1 Zero Calibration Check

Calibrate the O_2 electrochemical cell at 20.9 percent using fresh air. (20.9 percent O_2), free from ambient CO, NO_x , and other pollutants. Next, introduce the O_2 , CO, NO, and NO_2 zero calibration gas at the probe tip using the calibration assembly shown in Figure 1. During this check, do not make adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Set the flow rate to the value recommended by the manufacturer. Allow the electrochemical cell response to stabilize within \pm 5 percent of the mean reading, for at least thirty seconds one minute, before recording the result. After achieving a stable response, disconnect the gas and briefly purge with fresh air.

The zero level reading for CO, NO, and NO₂ shall be less than or equal to \pm 3 percent of the span gas value or \pm 1 ppm, whichever is less restrictive, and less than or equal to \pm 0.3 percent O₂ for the O₂ electrochemical cell.

3.3.2 Span Calibration Check

Individually inject each span gas into the analyzer at the probe tip using the calibration assembly. Allow the electrochemical cell response to stabilize within \pm 5 percent of the mean reading, for at least thirty secondsone minute, before recording the result. If the analyzer response for the CO, NO, or NO₂ electrochemical cells must be re-set during the pre-test calibration check,—(never during the post-test calibration check), following manufacturer's instructions. After achieving a stable response, disconnect the gas and briefly purge with fresh air. Repeat these steps for each span gas.

The span gas reading for the CO, and NO and NO electrochemical NOEC cells shall be withinless than \pm 5 percent of the span gas value and withinless than or equal to \pm 0.5 percent O₂ for the O₂ electrochemical cell. The span gas reading for NO₂ shall be less than \pm 10 percent of the span gas value to verify the equivalent concentration of 90 percent NO₂ recovery of span gas value as per AQMD Method 100.1.

3.4 POST-TEST CALIBRATION CHECK

After the Following each set of field emission tests, and within 10 calendar days of the last successful pre-test calibration check, perform the post-test calibration check in the same manner as the pre-test calibration check, (Sections 3.32.1 and 3.32.2.). If the emission test results are within 5 percent of engine's emission limits, then the post-test calibration must be performed immediately after the test period to verify compliance. Make no changes to the sampling system or analyzer calibration until the post-test calibration check has been recorded.

The difference between the pre-test calibration and post-test calibration span gas readings, which is defined as drift, shall not exceed \pm 5 percent for CO, NO and O₂. If the post-test calibration drift is greater than \pm 5 percent but less than \pm 10 percent check-for CO, NO and/or O₂ and the corrected concentration is less than 75% of the emission limit, then the test is considered valid for demonstrating compliance. Otherwise, the testing does not meet the specifications, all test data for that component are null and void, and recalibration and re-testing are required.

3.5 LINEARITY CHECK

Conduct the following procedure once for each nominal range that is to be used on each electrochemical cell, $(CO, NO, O_2 \text{ and } NO_2)$. Repeat the linearity check if an electrochemical cell is replaced. Linearity may be checked using a gas divider if it is calibrated according to EPA Method 205.

3.5.1 Linearity Check Procedure

Select a-mid-level calibration gases for CO, O_2 , NO, and NO₂ that are 40 to 60 percent of the nominal range. Follow the procedure for the Pre-Test Calibration Check, (Section $3.\underline{32.2}$) and then introduce the mid-level calibration gas for each electrochemical cell at the probe tip using the calibration assembly. During this check, do not make adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Set the flow rate to the value recommended by the manufacturer. Allow each reading to stabilize within \pm 5 percent of the mean reading, for at least thirty secondsoneminute, before recording the result. After achieving a stable response, disconnect the gas and briefly purge with fresh air.

Linearity shall be less than or equal to \pm 3 percent of the span gas concentration for NO, $\underline{O_2$, \underline{CO} and $\underline{NO_2}$ cells. \underline{CO} .

3.6 <u>STABILITY CHECK</u>

Conduct the following procedure once for each nominal range that is to be used on each electrochemical cell. (CO, NO, and NO_{2.}). Repeat the stability check if an electrochemical cell is replaced or exposed to gas concentrations greater than the analytical range of electrochemical cell specified by the manufacturer.

3.6.1 Stability Check Procedure

Energize sample pump and allow portable electrochemical analyzer to warm up to ambient temperature. Introduce the span gas for each electrochemical cell at the probe tip using the calibration assembly and record the analyzer response at least once per minute until the conclusion of the test. During this check, do not make adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Set the flow rate to the value recommended by the manufacturer. After the analyzer response has stabilized, continue to flow the gas for at least 30-minutes. At the end of the check, disconnect the gas and briefly purge with fresh air.

The analyzer response to CO, NO, and NO₂ span gases shall be less than or equal to ± 2.5 percent of the span gas value over a 30-minute period. As an alternative, the system will pass a stability check with less-or more than ± 1 percent of the span gas value over a 15-minute period.

3.7 CALCULATIONS

a. The following equation shall be used to determine the calibration error (E_{CAL}) for the zero and span calibration checks (Sections 3.2.1 and 3.2.2):

$$E_{CAL} = \left(\frac{AnalyzerResponse - Cal.GasConcentration}{Cal.GasConcentration}\right) \times 100\%$$

b. The following equation shall be used to determine the drift between the pre-test calibration and post-test calibration checks (Section 3.3):

Drift =
$$\left(\frac{\text{Post Test AnalyzerResponse} - \text{Pre Test AnalyzerResponse}}{\text{Pre Test AnalyzerResponse}}\right) \times 100\%$$

c. The following equations shall be used to determine the linearity (E_{LIN}) (Section 3.4.1):

$$E_{LIN} = \left(\frac{\text{Calculated Mid.- Mid. Span Gas Value}}{\text{Mid. Span Gas Value}}\right) \times 100\%$$

 $Calculated Mid. = (Slope \times Mid. Span Analyzer Response) + Zero Analyzer Response$

$$Slope = \left(\frac{Span Gas Value - Zero Value}{Span Gas Analyzer Response - Zero Analyzer Response}\right)$$

4.0 EMISSION TEST PROCEDURE

All engines shall be tested "as-found." No tuning or maintenance for the purpose of lowering tested emissions is allowed within 24 hours prior to testing or during testing.

4.1 SELECTION OF SAMPLING SITE AND SAMPLING POINTS

Select a sampling point located at least two stack diameters downstream of any disturbance (e.g. turbocharger exhaust, crossover junction, or recirculation take-off) and one-half stack diameter upstream of the gas discharge to the atmosphere. Typically, the existing sampling port will satisfy these conditions. Use a sample location at a single point near the center of the duct. If previous test data demonstrates that the stack gas concentration varies significantly across the duct diameter, greater than 10 percent, - (stratified stack gas concentrations), then traverse sampling shall be performed along one cross-sectional axis of the stack, using three points located at positions of 16.7, 50, and 83.3 percent of the stack diameter.

4.2 <u>ELECTROCHEMICALEC CELL TEMPERATURE AND FLOW MONITORING</u>

Do not interrupt the flow to the portable analyzer and maintain a constant sampling rate (± 1510) percent of the analyzer flow rate value experienced during the Pre-Test Calibration Check) during the entire test run. At no time shall the electrochemical cells be used outside the manufacturer's recommended operating range.

4.3 SAMPLE COLLECTION

Assemble the measurement system by following the manufacturer's recommended procedures for preparing and preconditioning the gas analyzer. Assure the system has no leaks and verify the gas scrubbing agent is not depleted. Zero the electrochemical analyzer with fresh air. Energize sample pump and allow portable electrochemical analyzer to warm up to ambient temperature.

Sample the stack gas for an equal period of time at each test point. At the start of the test, record the time, ambient <u>temperature</u>conditions, and operating condition of the engine. Record <u>emission</u> data at least every 15-seconds for a minimum of 15-minutes using procedures in Section 5.1.10 of CTM-030. Note that although at least 15-minutes of testing will be conducted, the actual sampling time will be greater, depending on the response time or stability time of the analyzer. Record the general operating conditions and load of the engine during the test. <u>Operating conditions include the parameters required to be monitored by the Inspection and Monitoring Plan.</u>

At the end of the test, conduct a post-test leak check of the measurement system, and then disconnect the gas and briefly purge with fresh air. If multiple engines are to be tested at a single facility, the post-test leak check may be postponed until after the last unit is tested. However, the analyzer shall be purged with fresh air between units, and if the measurement system fails the final post-test leak check, then all of the testing after the last successful leak check is null and void and re-testing is required.

4.4 CALCULATIONS AND DETERMINATION OF COMPLIANCE

The following procedure will determine the mean concentration of NO_x and CO_x (adjusted for calibration results and corrected to 15 percent O_{2x}) to determine compliance with Rule 1110.2 and equipment permit condition emission limits for each test.

- a. Determine the arithmetic mean of each gas concentration (NO, NO₂, CO and O₂) measured during the test period.
- b. The mean of each measured concentration (NO, NO₂, CO and O₂) shall be corrected using the following equation to give values adjusted for the pre-test calibration and post-test calibration results (C_{ADJ}):

$$C_{ADJ} = (C_{MEAS} - C_{CZ}) \times \left(\frac{C_{CAL} - C_{CZ}}{C_{CM} - C_{CZ}}\right)$$

Where: C_{ADJ} = -pollutant concentration adjusted for calibration, ppmdv

 C_{MEAS} = measured pollutant concentration, ppmdv

 C_{CAL} = span gas concentration, ppmdv

 C_{cz} = average concentration of the pre-test and post-test analyzer responses to zero gas, ppmdv

 C_{CM} = average concentration of pre-test and post-test analyzer responses to span gas, ppmdv

- c. Add NO and NO₂, together to determine NO_x.
- d. Compute the following formula using adjusted concentrations (C_{ADJ}) to determine compliance with emission limits for NO_x and CO:

$$N = (C_{ADJ}) \times \left(\frac{20.9 - 15}{20.9 - O_2}\right)$$

Where: $N = NO_x$ or CO concentration corrected to 15% O_2 , ppmdv

 C_{ADJ} = pollutant concentration of NO_x or CO adjusted per Section 4.4(b), ppmdv

 O_2 = oxygen concentration (%), dry basis, measured in the flue gas and adjusted per Section 4.4(b)

5.0 TESTING UNDER NON-IDEAL CONDITIONS

The following is a discussion of some common non-ideal testing conditions and their solutions in source testing:

5.1 LOAD CHANGES

If there are fluctuations in the process or operating conditions, such as changes in load, the testing may continue as long as the operating conditions are recorded to show each fluctuation. If the engine shuts down completely or if there are severe fluctuations during sampling, testing must be repeated for a minimum of 15 continuous minutes during acceptable operating conditions. All changes in process and operating conditions and test interruptions must be noted with the beginning and ending times of each occurrence on the field data sheets.

5.2 BYPASS STACK

If there are dampers or bypass stacks present, testing shall be conducted as follows:

a. If excess air is frequently introduced to the exhaust stack at a variable rate, concentration testing shall be performed while no excess air is introduced to the exhaust stack.

5.3 MULTIPLE STACKS

For multiple stacks, perform sampling at each of the stacks during acceptable testing conditions. Sampling at each stack need not be performed simultaneously.

5.4 OTHER NON-IDEAL TESTING CONDITIONS

If other non-ideal testing conditions exist (e.g. stack gas oxygen concentration greater than 19 percent), the facility must submit a source test protocol for review and written approval by the Executive Officer prior to testing.

6.0 RECORDKEEPING REQUIREMENTS

6.1 MEASUREMENT SYSTEM LOG

Maintain a bound log, available upon request, for each individual measurement system that includes the following records for 5 years. Electronically stored records are acceptable alternatives for 'hard copies' only if reproducible electronic and/or hard copies are retrievable upon request.

- a. Linearity and Stability Tests Recordkeeping Form (Form 1), which must be completed and signed by <u>trained personnel</u>. who has been certified per Rule 1110.2, <u>subparagraph (f)(1)(F)</u>.
- b. Calibration Recordkeeping Form (Form 2), which must be completed and signed by trained personnel who has been certified per Rule 1110.2, subparagraph (f)(1)(F).
- c. Certificates of analysis for all calibration gases listed on Forms 1 and 2.
- d. All maintenance and service records, including but not limited to dates that electrochemical cells and filters were replaced, and replacement parts purchase records.

6.2 ENGINE COMPLIANCE LOG

Maintain a bound log on-site, available for inspection at any time, which includes the following records for 5 years, as required by Rule 1110.2. Electronically stored records are acceptable alternatives for 'hard copies' only if reproducible electronic and/or hard copies are immediately retrievable for inspection at any time.

- a. <u>Periodic Monitoring Emissions Test</u> Recordkeeping Form (Form 3), which must be completed and signed by <u>trained personnel</u>, who has been certified per Rule 1110.2, <u>subparagraph (f)(1)(F)</u>.
- b. Source test reports, including those required per Rule 1110.2., subparagraph (f)(1)(C).
- c. Inspection and Monitoring Plan. records. per Rule 1110.2, subparagraph (f)(1)(D).
- d. Operating Log per Rule 1110.2, subparagraph (f)(1)(E).

7.0 REPORTING REQUIREMENTS

If any testing conducted according to this protocol or according to Rule 1110.2, paragraph (g), determines that emissions concentrations have exceeded either Rule 1110.2 or equipment permit condition emission limits, the operator shall comply with the following requirements (as per Rule 1110.2, clause (f)(1)(D)(vii)):

- a. Notify the District at 1-800-CUT-SMOG within one hour of learning of the exceedance in the same manner required by paragraph (b)(1) of Rule 430;
- b. Immediately correct the noncompliance or shut down the engine within 24 hours or the end of an operating cycle, whichever is sooner, in the same manner as required by clause (b)(3)(A)(iv) or Rule 430; and

c. Comply with all <u>other</u> requirements of Rule 430 if there was a breakdown.



FORM 1
Linearity and Stability Tests Recordkeeping Form



FORM 2
Calibration Recordkeeping Form



FORM 3

<u>Periodic Monitoring Emissions Test</u> Recordkeeping Form



ATTACHMENT I

EPA CONDITIONAL TEST METHOD CTM-030